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Liquid phase process for the polymerization of alpha-olefins

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## Liquid phase process for the polymerization of alpha-olefins

The present invention relates to a liquid-phase process for the polymerization of  $\alpha$ -olefins. In particular, it relates to a process for the polymerization of  $\alpha$ -olefins, especially of butene-1, in liquid phase followed by a post-polymerization step where the catalyst residues are deactivated with a high efficiency.

Butene-1 (co)polymers are well known in the art and are mainly used in the manufacture of molded products such as pipes, packaging films, adhesives.

Hitherto, butene-1 (co)polymers have been mainly produced by solution polymerisation and slurry polymerisation in the presence of coordination catalysts which are generally referred to as Ziegler-Natta catalysts. When a solution process is adopted, the polymerisation is generally carried out in liquid butene-1 at conditions under which a solution of polybutene in butene-1 is discharged from the polymerisation reactor. When a slurry polymerisation is adopted, the polymerisation is carried out in liquid butene-1 at conditions under which the polymer is produced as a solid, thus obtaining a slurry of solid polymer in butene-1. In both cases, an additional step is required wherein the obtained polymer is separated from the monomer, which is recovered and re-circulated to the reactor.

Several generations of Ziegler-Natta catalysts have been used in the production of isotactic polyolefins, such as polypropylene or polybutene. A former generation of Ziegler-Natta catalysts employed in the polymerisation of butene-1 is based on  $\text{TiCl}_3$  as the catalyst component. Butene-1 (co)polymers have been prepared by polymerising butene-1 in the presence of  $\text{TiCl}_3$  based catalyst and of a dialkyl aluminum halide as the cocatalyst. In view of the relatively low activity of said catalyst systems, the obtained polymer has a high content of catalyst residues (generally more than 300 ppm of Ti). Such a high content of catalyst residues is detrimental to the final properties of the polymers, so as to require a deashing step in order to extract the catalyst residues from the polymer. The deashing step is generally carried out in a deashing chamber by contacting the solution or slurry containing polybutene with caustic water. Afterwards, catalyst salts and water are separated from the polymeric phase by gravity in a settler: catalyst salts and water are then discharged from the settler, so that the content of catalyst residues in the polybutene solution

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or slurry is minimized. This deashing step involves the use of a large amount of liquids and increases the complexity of the reaction plant. Furthermore, a complete separation of the water from the polymeric phase is hardly achievable in the settling step and droplets of water remain in the polymer solution.

The above problems have been overcome by using stereospecific Ziegler-Natta catalysts of a more recent generation which have been developed particularly for the production of isotactic polypropylene. These catalysts typically comprise a support of magnesium chloride combined with  $\text{TiCl}_4$  and an electron donor, such as ethyl benzoate. The cocatalyst is again an aluminium alkyl, typically an aluminium trialkyl compound. When  $\alpha$ -olefins of three or more carbon atoms are polymerised in the presence of said catalysts, stereoregular polymers are obtained with a high polymerisation yield. In view of the high activity, the content of catalyst residues in the polymerisation product is drastically reduced. Generally the final polymer contains less than 20 ppm of Ti. As a consequence, the removal of catalyst residues from the polymer can be omitted, thus improving greatly the simplicity of the process and reducing operative costs in the plant. However, a liquid-phase polymerisation of butene-1 necessarily requires the separation of the obtained polybutene from the unreacted monomer. The monomer recovery is generally carried out in a separation step wherein high temperatures, of about 150-250°C, are requested. Before such separation step, a deactivation of the catalyst is therefore necessary in order to avoid an undesired modification of the properties of the final polymer due to a further uncontrolled polymerisation and/or a thermal degradation of the polymer. Unless the catalyst is deactivated, the final pellets could have a higher melt index and a different molecular weight distribution with respect to the polymer obtained at the outlet of the polymerisation step. Such a melt index shift should be prevented in order to obtain a final polymer having the desired properties.

The methods known in the art generally refer to a deactivation of the catalyst carried out by introducing a deactivator compound during the polymerization step. For instance, in a multi-stage polymerization process for producing an impact copolymer composition, the relative proportions of homopolymer phase and copolymer phase can be controlled by the addition of suitable catalyst deactivators which kill or reduce catalyst activity. Such catalyst deactivators are generally introduced at a point situated between the first and the second polymerisation reactor or directly to the second reactor. An example of this (FE6027\_EP)

deactivation is given in EP 225,099 where the properties of a polypropylene impact copolymer are said to be improved by introducing a polyalkylene glycol ether as a catalyst deactivator between the first and second polymerisation step. As a consequence of this addition, the catalyst activity in the second stage polymerisation catalyst is reduced from 30% to 80%.

When a liquid-phase polymerisation of an  $\alpha$ -olefin has to be followed by the separation of the obtained polymer from the unreacted  $\alpha$ -olefin, as it is the case for the polymerization of butene-1, the prior art teachings are not satisfactory in order to solve the problems correlated to the deactivation of the catalyst system.

It is known the use of low molecular weight gases or liquids in order to reduce the catalyst activity to a level where the polymerisation stops. The use of water as a Ziegler-Natta catalyst killer is disclosed in USP 4,701,489 that refers to a method of deactivating catalyst residues in amorphous polyalphaolefins, such as amorphous propylene homo- and copolymers. After a bulk polymerisation process and a separation of the unreacted monomers from the molten polyalphaolefin, a deactivation of the catalyst residues contained in the molten polyalphaolefin is described. According to the patent, the deactivation is carried out by contacting the molten amorphous polyalphaolefin with at least 3 moles of water per mole of aluminium present in the polymer.

Water and similar low-boiling compounds, such as  $\text{CO}_2$  and alcohols, are recognised to be high-efficiency deactivators of Ziegler-Natta catalysts. However, when a liquid-phase polymerisation of  $\alpha$ -olefin is followed by a step for separating the obtained polymer from the unreacted  $\alpha$ -olefin, these low boiling compounds will collect together with the unreacted monomer. As a consequence, a further separation between these deactivators and the unreacted  $\alpha$ -olefin is necessary in order to avoid an entry of the deactivator directly in the polymerisation reactor and a consequent termination of the polymerisation reaction. However, the above-mentioned compounds are generally not easily separable from the unreacted  $\alpha$ -olefin. In fact, conventional distillation units are not sufficient to achieve an acceptable separation and molecular sieves must be provided in order to capture these deactivators and to complete efficiently the separation. The use of molecular sieves increases the complexity of the process and the operative costs in the monomer recovery section.

In view of the above, an appropriate catalyst deactivation in a liquid-phase polymerisation process for producing polyolefins should contemplate an easy separation of the deactivator from the unreacted monomer and, at the same time, should cause no modification of the desired properties of the obtained polyolefin.

It would be desirable to provide a liquid-phase process for polymerizing  $\alpha$ -olefins wherein the catalyst residues are deactivated without causing any worsening in the final properties of the obtained polymer and improving the recovery of the monomer in the recovery section.

The Applicant has surprisingly found a liquid-phase process for polymerizing  $\alpha$ -olefins, which combines the above advantages with a high efficiency in the deactivation of the catalyst residues.

It is an object of the present invention a liquid-phase process for polymerizing  $\alpha$ -olefins of the formula  $\text{CH}_2=\text{CHR}$ , where R is H or an alkyl radical C1-C6, to produce a polymer that is soluble in the reaction medium, comprising the steps of:

- a) continuously polymerising in liquid phase the  $\alpha$ -olefin in the presence of a catalyst based on a transition metal compound;
- b) continuously withdrawing from step a) a solution of the polymer in the liquid reaction medium;
- c) mixing in one or more mixing stages said solution of the polymer in the reaction medium with an organic compound having: at least a hydroxy group, a boiling point higher than  $150^\circ\text{C}$ , and a ratio between the molecular weight (MW) and the number of hydroxy groups ( $n_{\text{OH}}$ ) comprised between 20 and 100.

The process of the present invention will be described in detail with reference to a liquid-phase process for homo- or co-polymerizing butene-1, where in step a) a solution of polybutene-1 (PB-1) in the reaction medium is obtained. The polymerization step a) takes place in liquid phase in the presence or absence of an inert hydrocarbon solvent. Suitable solvents can be liquid hydrocarbons having 5 to 10 carbon atoms, such as pentane, hexane, heptane, octane, etc. Preferably liquid butene-1 is used as the reaction medium in the process of the invention: the solution process is feasible since polybutene-1 can dissolve in butene-1 at relatively low pressures. Furthermore, the two components of the solution perfectly mix together at the optimum working temperatures of Ziegler-Natta and metallocene catalysts. In order to obtain the best performance of the catalyst together (FE6027\_EP)

with a complete miscibility of monomer and polymer, the polymerization temperature is generally kept at a value comprised in the range of from 65 to 85°C while the pressure is generally comprised between 8 and 40 bar. Preferred operating conditions are at temperatures of from 70 to 80°C and at a pressure comprised between 12 and 25 bar.

The presence of a highly active catalyst of the Ziegler-Natta or metallocene type is involved in step a). A high polymerization yield is thus achieved, ranging from 8-200 kg of PB-1 for gram of catalyst. Accordingly, the amount of catalyst residues in the obtained polybutene-1 is negligible, generally lower than 120 ppm, and do not adversely affect the quality of the final polymer. A product of high industrial value having an excellent hue and strength is obtained without carrying out any removal of the catalyst residues from the polymer.

It is preferred to carry out a pre-contact of the catalyst components in a pre-contacting pot. A transition metal compound, an aluminum alkyl compound and optionally an electron donor compound are brought into contact at a temperature lower than 60°C, preferably comprised between 0 and 20°C. The catalyst system formed in the pre-contacting pot is then transferred to the first polymerization reactor. Optionally a pre-polymerization step can be interposed between the pre-contact of the catalyst components and the polymerization reactor.

The polymerization step a) can be performed in one or more continuously stirred tank reactors, wherein a high-viscosity polymeric solution of polybutene-1 in butene-1 is formed. It is preferred to carry out the polymerization under such conditions that the concentration of the polymer in the solution does not become unduly high, as otherwise the polymeric solution would become too viscous and difficult to stir and/or process. The polymer concentration is suitably kept to a value of less than 35% by weight. In fact, a further increase of the polymer concentration would make the viscosity of the polymeric solution too high and the stirring device of the reactors could be blocked. Low concentrations are quite easy to process but uneconomic due to the low productivity of the plant and the high influence of utilities costs. Therefore, the polymerization is preferably conducted in such a way that the concentration of polybutene-1 in butene-1 is comprised between 10 and 30% by weight, more preferably between 20 and 30% by weight.

Optionally, butene-1 may be polymerized in the presence of up to 20% by weight,

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preferably 0.5-10% by weight, based on butene-1, of another  $\alpha$ -olefin. Suitable comonomers are, for instance, ethylene, propylene, pentene-1 and hexene-1.

In the case of multiple stirred reactors arranged in series, different working conditions can be adopted in each reactor, as regards the concentration of molecular weight regulator, monomer, comonomer. Accordingly, polybutene of different average molecular weight can be obtained in each stirred reactor, thus leading to a final product having a broad molecular weight distribution (MWD). Hydrogen can be advantageously used to control the polymer molecular weight. The use of  $H_2$  as a chain transfer agent increases the catalytic activity of the polymerization process.

The total residence time in polymerization step a) is generally comprised between 1 and 4 hours, preferably between 2 and 3 hours.

The above specified values of temperature must be maintained inside each reactor by means of a suitable cooling system. In order to balance the heat produced by the polymerization reaction, a heat exchange unit is placed along the recycle loop to the reactor. According to an embodiment, the solution of polybutene in butene-1 can be withdrawn from the bottom of the stirred reactor by means of a suitable pump for high viscosity fluids, such as a gear pump or a screw pump, and then the major portion thereof is passed through the heat exchanger unit to remove heat of reaction and returned to the reactor. The remaining portion is directly fed to the successive polymerization reactor.

At the outlet of the last stirred tank reactor, the obtained solution of PB-1 in butene-1 is transferred to the deactivation step c). It is important to point out that the deactivation step cannot be effected by a simple addition of the deactivator to the polymeric solution coming from the polymerization. This is a consequence of the remarkable difference existing between the viscosity of the killer compounds and the viscosity of the polymeric solution to be deactivated. In fact, the two streams differ in viscosity by several orders of magnitude: the viscosity of the polymeric solution is of about 1000-100000 cP, while the viscosity of the killer compounds is of about 1-100 cP. In view of such difference, the killer compounds can reach uniformly all the catalyst sites and thus deactivate efficiently the catalyst only if an intense and effective mixing of the components is provided. This intimate mixing can be achieved in one or more mixing tanks placed in series or, alternatively, in a single deactivation apparatus equipped with a sequence of more mixing stages where a high shear rate is established.



As above indicated, the deactivator compounds of the present invention are compounds having a boiling point higher than 150°C and at least a hydroxy group. In particular, they are characterized by a suitable ratio between the molecular weight (MW) and the number of hydroxy groups ( $n_{OH}$ ). Said ratio  $MW/(n_{OH})$  should be comprised between 20 and 100, preferably between 30 and 70. Preferred deactivator compounds satisfying the above requirements are, for example, propylen glycol, dipropylen glycol, glycerol, diethylen glycol and butandiol.

Such compounds show a high efficiency in deactivating the catalyst system even if a small amount thereof is used. For instance, in order to deactivate a Ziegler-Natta catalyst comprising a Ti-based solid catalyst component and an Aluminum compound as an activator, it is sufficient to use the above compounds with a molar ratio deactivator/(Ti+Al) higher than  $2/n_{OH}$ , wherein  $n_{OH}$  is the number of hydroxy groups of the deactivator compound. For instance, in the case of propylenglycol ( $n_{OH}=2$ ) a molar ratio deactivator/(Ti+Al) higher than 1 should be provided. Preferably, the above-defined molar ratio is comprised between  $3/n_{OH}$  and  $6/n_{OH}$ . The deactivator may be added as such or dispersed in a liquid medium, such as an aliphatic hydrocarbon.

According to a preferred embodiment of the present invention, a specific apparatus has been designed in order to ensure an intimate contact between the polymeric solution of PB-1 in butene-1 and the stream containing the deactivator compound. This apparatus comprises a stirring shaft provided with impellers in a number comprised between 2 and 20, preferably between 4 and 12: as a consequence, more mixing stages are formed along the shaft by the rotation of each impeller. The impellers are equipped with radial blades fixed at the stirring shaft, said radial blades causing a radial flow inside each mixing stage. The polymeric solution and the deactivator are continuously fed at the inlet of this apparatus and slowly flow through the sequence of mixing stages. The multi-stage vigorous agitation forms a high-shear field and ensures an intimate contact and a strong mixing of the components: baffles are provided along the vertical wall of the apparatus in order to increase the shear rate. Together with the radial flow imposed by the rotation of the blades inside each mixing stage, an axial piston-like flow is involved by the sequence of mixing stages along the shaft and by the complete filling of the apparatus by the liquid components.

Besides providing a high efficiency in the deactivation of the catalyst components, thus

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preventing any further uncontrolled, undesired polymerisation or polymer degradation downstream the polymerization reactor, the use of the deactivators compounds of the invention ensures other remarkable advantages which may be summarized as follow:

- 1) Differently from the known low-boiling deactivators, such as water, methanol, etc. these compounds are more easily separable from the unreacted butene-1 in the successive step wherein the unreacted monomer is separated from the polymer.
- 2) Another remarkable property of these compounds reveals particularly suitable when the polymer is aimed to be used in medical applications or in food packaging applications: these compounds comply with the provisions of the European Directive 90/128 and following amendments. As a consequence, the presence of them inside the final polymer after the pelletization is not detrimental for the use of the obtained polyolefin in the above-cited applications.

After the deactivation of the catalyst residues, the solution of polybutene in butene-1 is passed to a separation step, wherein the polybutene-1 is separated from the unreacted monomer, which is recovered and re-circulated to the polymerization step a). The removal of the unreacted monomer from the polymer can be carried out according to methods known in the art. Preferably it is adopted a melt devolatilization technique using one or more volatilization chambers operating at a decreasing pressure. For instance, two volatilizers placed in series can be used, the first one operating under pressure and the second one operating under vacuum. By this technique a polybutene melt substantially free of monomer is obtained. Afterwards, the polymer melt is compounded forcing it to flow inside a static mixer to which the master batch is added.

As regards the monomer recovery section, the gaseous phase separated from the polymer can contain, besides butene-1, also a little amount of the catalyst deactivators, so that the monomer recovery requires the separation of said compounds from butene-1. Generally, the above separation can be efficiently carried out by the use of two distillation units, thus preventing the introduction of the deactivators inside the polymerization reactors.

As regards the catalyst used in polymerization step a), Ziegler-Natta catalysts are the preferred one. They comprise a titanium compound supported on magnesium chloride in active form and an alkylaluminum compound as the cocatalyst. When an internal electron-donor compound is used, also a high stereospecificity is achieved.

The preferred titanium compounds used as a transition metal compound are  $\text{TiCl}_4$  and  $\text{TiCl}_3$ . Also Ti-haloalcoholates of formula  $\text{Ti}(\text{OR})_n\text{X}_y$ , where  $n$  is the valence of titanium and  $y$  is a number between 1 and  $n$ , can be used. The internal electron-donor compound may be selected from esters, ethers, amines and ketones. It is preferably selected from alkyl, cycloalkyl or aryl esters of monocarboxylic acids, for example benzoic acid, or polycarboxylic acids, for example phthalic or malonic acid, the said alkyl, cycloalkyl or aryl groups having from 1 to 18 carbon atoms. Examples of the said electron-donor compounds are methyl benzoate, ethyl benzoate and diisobutyl phthalate. Generally, the internal electron donor compound is used in molar ratio with respect to the  $\text{MgCl}_2$  of from 0.01 to 1 preferably from 0.05 to 0.5.

The alkyl aluminum compound is preferably chosen among trialkyl aluminum compounds, such as for example triethylaluminum, triisobutylaluminum, tri-*n*-butylaluminum, tri-*n*-hexylaluminum, tri-*n*-octylaluminum. It is also possible to use mixtures of trialkylaluminum's with alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as  $\text{AlEt}_2\text{Cl}$  and  $\text{Al}_2\text{Et}_3\text{Cl}_3$ .

The external donor can be of the same type or it can be different from the internal donor described above. Suitable external electron donor compounds include silicon compounds, ethers, esters, amines, heterocyclic compounds and particularly 2,2,6,6-tetramethyl piperidine, ketones and the 1,3-diethers. Another class of preferred external donor compounds is that of silicon compounds of formula  $\text{R}_a^5\text{R}_b^6\text{Si}(\text{OR}^7)_c$ , where  $a$  and  $b$  are integer from 0 to 2,  $c$  is an integer from 1 to 3 and the sum  $(a+b+c)$  is 4;  $\text{R}^5$ ,  $\text{R}^6$ , and  $\text{R}^7$ , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms. Particularly preferred are the silicon compounds in which  $a$  is 0,  $c$  is 3,  $\text{R}^6$  is a branched alkyl or cycloalkyl group, optionally containing heteroatoms, and  $\text{R}^7$  is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, *t*-butyltrimethoxysilane and hexyltrimethoxysilane. The electron donor compound is used in such an amount to give a molar ratio between the organoaluminum compound and said electron donor compound of from 0.1 to 500, preferably from 1 to 300 and more preferably from 3 to 100.

The above mentioned objects and advantages of the present invention will become evident from the following description of the accompanying drawings. It is to be understood that the enclosed drawings have only an illustrative purpose, not restrictive of the scope of the invention.

One preferred embodiment of the process of the invention is described in detail with reference to the accompanying Figure 1.

With reference to Fig. 1, a transition metal compound, an aluminum alkyl compound and optionally an electron donor compound are fed via line 11 to a pre-contacting pot 20. The catalyst system formed in the pre-contacting pot is then transferred via line 12 to a first continuously stirred tank reactor 30 together with a stream 13 containing butene-1, hydrogen and optionally comonomers. Hydrogen and comonomers are fed to the reactors through line 14 and 17, while liquid butene-1 is introduced by means of lines 15 and 16. In particular, the monomer coming from the recovery section is provided by line 16, while fresh butene-1 is fed by line 15.

The polymerization step a) takes place in two continuously stirred tank reactors indicated with 30 and 60. The operating conditions in the two reactors are selected as above indicated and a high-viscosity solution of polybutene-1 in butene-1 is formed in both the reactors.

Lines 14 and 17 can provide a different amount of  $H_2$  as well as different types and amounts of comonomers, so that butene-1 (co)polymers with a different composition and different average molecular weight can be produced in the reactors 30 and 60. This 2-stage bimodal polymerization has the advantage of modulating the polymerization in the two reactors so as to produce a final product having the desired breadth of molecular weight distribution (MWD), also tailoring the other polymer properties, such as melting point, flexural modulus, etc.

The hydrogen concentration in the first reactor 30 is generally kept at a level lower than the hydrogen concentration in the second reactor 60. As a consequence, polybutene-1 are obtained in the first reactor with a melt flow index generally lower than the polymers formed in the second reactor.

The obtained solution of polybutene in butene-1 is withdrawn from the bottom of reactor 30 by means of a gear pump 40, the major portion thereof being fed through line 18 to a heat exchanger unit 50 and then returned to reactor 30. The remaining portion is directly fed through line 19 to the second polymerization reactor 60. The solution of polybutene in butene-1 is withdrawn from the bottom of reactor 60 by means of another gear pump 70, the major portion thereof being fed through line 20 to a second heat exchanger unit 80 and then returned to reactor 30. The remaining portion of the polymeric solution is

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directly fed through line 21 to the top of the deactivation apparatus 90 for the killing of the catalyst residues. At the same time, one or more deactivator compounds according to the invention are continuously fed through line 22 to the top of a deactivation apparatus 90. The polymeric solution, once deactivated, is withdrawn from the bottom of the deactivation apparatus 90 and fed to the separation section via line 23. In the separation section a polybutene melt is separated from the unreacted monomer. The deactivator compounds of the invention will partially collect in line 24 together with unreacted butene-1, the rest will remain entrapped inside the polymer melt. The unreacted butene-1 is then separated by distillation from the deactivator compounds in the recovery section and then recycled to the polymerization step through line 16. The obtained polybutene-1 melt is first compounded with suitable additives and then subjected to underwater pelletization (not shown in Fig. 1).

A preferred embodiment of the deactivation apparatus used in the process of the invention is shown in Figure 2. This apparatus comprises a stirring shaft 1 provided with impellers equipped with radial blades 2. Mixing stages are formed along the shaft by the rotation of each impeller. Baffles 3 are provided along the vertical wall of the apparatus in order to increase the shear rate. The polymeric solution 4 and the deactivator 5 are continuously introduced at the top of the apparatus and slowly flow through the sequence of mixing stages. Together with the radial flow imposed by the rotation of the blades inside each mixing stage, also an axial piston-like flow is achieved along the shaft. The deactivated polymer solution 6 is withdrawn from the bottom of the apparatus and passed to the separation step.

The following examples have to be considered representative and non-limiting of the scope of the invention.

#### EXAMPLES

The following examples relate to some tests carried out in a pilot plant and aimed at evaluating the effectiveness of the deactivator compounds of the invention when used in a liquid phase process for polymerizing butene-1.

The polymerization tests were carried out into two continuously stirred tank reactors having a volume of 0,33 m<sup>3</sup> placed in series according to the embodiment of Fig.1. The catalyst residues were deactivated in a deactivation apparatus according to the embodiment of Fig.2.

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The polymerization was carried out in the presence of a catalyst comprising:

- a solid catalyst component based on a Titanium compound;
- triisobutylaluminum (TIBA) as a catalyst activator;
- hexyltrimethoxysilane as a donor compound.

The Melt Flow Index of the obtained polybutene-1 was measured by using a weight of 2,16 Kg at 190°C according to ISO 1133 (ASTM D1238 condition E).

#### Preparation of the solid catalyst component

Into a 500 ml four-necked round flask, purged with nitrogen, 225 ml of  $\text{TiCl}_4$  were introduced at 0°C. While stirring, 6,8 g of microspheroidal  $\text{MgCl}_2 \cdot 2,7\text{C}_2\text{H}_5\text{OH}$  (prepared as described in Ex. 2 of USP 4,399,054 but operating at 3.000 rpm instead of 10,000) were added. The flask was heated to 40°C and 4.4 mmoles of diisobutylphthalate were thereupon added. The temperature was raised to 100°C and maintained for two hours, then stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

200 ml of fresh  $\text{TiCl}_4$  were added, the mixture was reacted at 120°C for one hour then the supernatant liquid was siphoned off and the solid obtained was washed six times with anhydrous hexane (6 x 100 ml) at 60°C and then dried under vacuum. The catalyst component contained 2.8 wt% of Ti and 12.3 wt% of phthalate.

#### Example 1

##### - Polymerization -

0,5 g/h of the above solid catalyst component (corresponding to  $0,15 \cdot 10^{-3}$  mol/h of Ti), 50 g/h of TIBA (corresponding to 0,25 mol/h of Al) and 0,3 g/h of hexyltrimethoxysilane were pre-contacted in hexane at 15°C for 10 minutes before the feeding to the first reactor. Liquid butene-1 together with  $\text{H}_2$  as a molecular weight regulator were continuously fed to the polymerization reactors. The polymerization conditions in the first and second reactor are reported in Table 1 as well as the feeding ratio  $\text{H}_2/\text{C}_4\text{H}_8$ .

TABLE 1

Polymerization conditions	1 <sup>st</sup> Reactor	2 <sup>nd</sup> Reactor
Temperature (°C)	70	75
Pressure (bar)	20	20
Residence Time (min)	160	80
H <sub>2</sub> /C <sub>4</sub> H <sub>8</sub> (ppm weight)	2	80

A solution of polybutene in butene-1 having a polymer concentration of 25% by weight was continuously withdrawn from the second reactor at a flow rate of 160 kg/h. This means a polymer production of 40 kg/h and a catalyst activity of 130 kg of polymer for each gram of solid catalyst component. A sample of polymeric solution was taken at the outlet of the second reactor in order to evaluate the Melt Flow Index of the obtained polybutene-1: a value of 0,40 was measured.

#### Deactivation -

The solution of PB-1 in butene-1 was passed to the deactivation apparatus for the killing of the catalyst residues. Propylene glycol was used as a deactivator compound.

Propylen glycol



Boiling point:

185°C

Molecular Weight (MW):

76

MW/ $\rho_{\text{OH}}$ :

38

50 g/h of  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$  (corresponding to 0.66 mol/h) were continuously fed to the top of the deactivation apparatus together with 160 kg/h of polymeric solution. The molar ratio between the propylene glycol and the moles of (Ti+Al) of the catalyst was equal to 2,6.

#### Separation and monomer recovery -

After the deactivation step, the solution of polybutene in butene-1 was heated up to 210°C and then transferred into two devolatilization chambers placed in series, the first one operating at 6 bar, the second one operating at 50 mbar. Polybutene-1 melt with a negligible amount of monomer was withdrawn from the bottom of the second volatilizer, while a gaseous mixture containing butene-1 and propylene glycol was collected at the top of the first volatilizer.

The unreacted monomer was recovered by means of two distillation columns and then (FE6027\_EP)

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returned to the polymerization section. No change in the polymerization yield was observed.

At the outlet of the second volatilizer, the PB-1 melt was additivated with Irganox 1010 as an antioxidant compound and then transferred to an underwater pelletizer.

The measure of the Melt Flow Index of the obtained pellets was of 0,45. Accordingly, the process of the invention ensures a limited and negligible Melt Flow Index shift and combines a high polymerization yield with a high efficiency in the deactivation of the catalyst residues.

### Example 2

#### Polymerization -

0,18 g/h of the solid catalyst component (corresponding to  $0,054 \cdot 10^{-3}$  mol/h of Ti), 46 g/h of TIBA (corresponding to 0,23 mol/h of Al) and 0,5 g/h of hexyltrimethoxy-silane were pre-contacted in hexane at 15°C for 10 minutes before the feeding to the reactors. H<sub>2</sub> was used as a molecular weight regulator. Liquid butene-1 and ethylene were continuously fed to the polymerization reactors according to the feeding ratios reported in Table 2. The polymerization conditions in the first and second reactor are reported in Table 2.

TABLE 2

Polymerization conditions	-1 <sup>st</sup> Reactor	2 <sup>nd</sup> Reactor
Temperature (°C)	70	75
Pressure (bar)	24	24
Residence Time (min)	135	80
C <sub>2</sub> H <sub>4</sub> /C <sub>4</sub> H <sub>8</sub> (% wt)	0,15	0,18
H <sub>2</sub> /C <sub>4</sub> H <sub>8</sub> (ppm weight)	11	200

A solution of a random copolymer in butene-1 having a polymer concentration of 17% by weight was continuously withdrawn from the second reactor at a flow rate of 155 kg/h. This means a polymer production of 26 kg/h and a catalyst activity of 140 Kg of polymer for each gram of solid catalyst component. A sample of polymeric solution was taken at the outlet of the second reactor in order to evaluate the Melt Flow Index of the obtained polybutene-1: a value of 0,75 was measured.

#### Deactivation -

The solution of modified PB-1 in butene-1 was passed to the deactivation apparatus for (FE6027\_EP)



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the killing of the catalyst residues. 50 g/h of propylene glycol (corresponding to 0.66 mol/h) were continuously fed to the top of the deactivation apparatus together with 155 kg/h of polymeric solution. The molar ratio between the propylene glycol and the moles of (Ti+Al) of the catalyst was equal to 2,86.

#### Separation and monomer recovery -

The same operative conditions of Example 1 were carried out.

The unreacted butene-1 was recovered by means of two distillation columns and then returned to the polymerization section. No change in the polymeration yield was observed.

At the outlet of the second volatilizer, PB-1 melt was withdrawn and transferred to an underwater pelletizer. The measure of the Melt Flow Index of the obtained pellets was of 0,90 so that a negligible MI shift was observed.

#### Example 3

##### Polymerization -

The polymerization was carried out in a single continuously stirred tank reactor having a volume of 0,33 m<sup>3</sup>.

0,25 g/h of the solid catalyst component (corresponding to 0,075 10<sup>-3</sup> mol/h of Ti), 38 g/h of TIBA (corresponding to 0,19 mol/h of Al) and 0,7 g/h of hexyltrimethoxy-silane were pre-contacted in hexane at 15°C for 10 minutes. Liquid butene-1 together with H<sub>2</sub> as a molecular weight regulator were continuously fed to a polymerization reactor. The polymerization conditions are reported in Table 3.

TABLE 3

Polymerization conditions	-1 <sup>st</sup> Reactor
Temperature (°C)	75°C
Pressure (bar)	22
Residence Time (min)	180
H <sub>2</sub> /C <sub>4</sub> H <sub>8</sub> (ppm weight)	20

A solution of PB-1 in butene-1 with a concentration of 25% by weight was continuously withdrawn from the second reactor at a flow rate of 60 kg/h. This means a polymer production of 15 kg/h and a catalyst activity of 60 kg of polymer for each gram of solid catalyst component. A sample of polymeric solution was taken at the outlet of the second (FE6027\_EP)

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reactor in order to evaluate the Melt Flow Index of the obtained polybutene-1: a value of 0,40 was measured.

#### **Deactivation -**

The solution of PB-1 in butene-1 was passed to the deactivation apparatus for the killing of the catalyst residues. Dipropylene glycol was used as a deactivator compound.

Dipropylene glycol  $\text{HOC}_3\text{H}_6\text{OC}_3\text{H}_6\text{OH}$

Boiling point:  $230^\circ\text{C}$

Molecular Weight (MW): 134

MW/ $\text{noH}$  : 67

88,4 g/h of dipropylene glycol (corresponding to 0,66 mol/h) were continuously fed to the top of the deactivation apparatus together with 160 kg/h of polymeric solution. The molar ratio between the propylene glycol and the moles of (Ti+Al) of the catalyst was equal to about 3,5.

#### **Separation and monomer recovery -**

The same operative conditions of Example 1 were carried out.

The unreacted monomer was recovered by means of two distillation columns and then returned to the polymerization section. No change in the polymerization yield was observed.

At the outlet of the second volatilizer, PB-1 melt was withdrawn and transferred to an underwater pelletizer. The measure of the Melt Flow Index of the obtained pellets was of 0,50 so that a negligible MI shift was observed.

#### **Example 4 (comparative)**

##### **Polymerization -**

The polymerization of butene-1 was carried out according to the same conditions of example 1. A sample of polymeric solution was taken at the outlet of the second reactor and a melt flow index of 0,40 was measured.

##### **Deactivation -**

The polymeric solution withdrawn from the second reactor was not subjected to any deactivation treatment of the catalyst residues.

##### **Separation and monomer recovery -**

The same operative conditions of Example 1 were carried out. At the outlet of the second volatilizer polybutene-1 melt was transferred to the underwater pelletizer.

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The melt index of the obtained pellets was of 3,0 so that an unacceptable shift of the melt index was observed. This example proves that a liquid-phase polymerisation of butene-1 must be followed by a deactivation treatment of the catalyst residues to avoid, during the separation step, uncontrolled and undesired side reactions or a polymer degradation, which can modify the final structure of the polymer.

#### **Example 5 (comparative)**

##### **Polymerization -**

The polymerization of butene-1 was carried out according to the same conditions of example 1, so that a value of  $MI=0,40$  was measured at the outlet of the second reactor.

##### **Deactivation -**

The solution of PB-1 in butene-1 was passed to the deactivation apparatus for the killing of the catalyst residues. As a deactivator, a mixture of alkyl diethanolamines of formula  $R-N(CH_2CH_2OH)_2$  wherein R is an alkyl radical  $C_{12}-C_{18}$  was used (ATMER 163 traded by Atlas Chemical Industries).

Mixture of alkyl diethanolamines	$R-N(CH_2CH_2OH)_2$	$R=C_{12}-C_{18}$
Molecular Weight (MW):	271-357	
MW/ $n_{OH}$ :	135-178	

0.66 mol/h of Atmer 163 were continuously fed at the top of the deactivation apparatus together with 160 kg/h of polymeric solution. The ratio between the moles of Atmer 163 and the moles of (Ti+Al) was of 2,6.

##### **Separation and monomer recovery -**

The same operative conditions of Example 1 were carried out.

At the outlet of the second volatilizer polybutene-1 melt was transferred to the underwater pelletizer. The melt index of the obtained pellets was of 1,0 so that a shift of the melt index was observed. Moreover, it was detected an amount of about 3.000 ppm (weight) of the above deactivator in the PB-1 pellets. Such amount is generally not acceptable in all the applications where a polymer with a high degree of purity is requested. This examples proves that a compound having a ratio  $MW/n_{OH}$  higher than 100 is not suitable to kill the catalyst residues contained in a polymeric solution obtained from a liquid-phase polymerisation of butene-1.

The deactivation conditions, as well as the values of Melt Index in the examples 1-5 are reported in Table 4, wherein the Melt Index at the outlet of the polymerization step is

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indicated with  $MI^{(A)}$ , while the Melt Index of the final pellets is indicated with  $MI^{(B)}$ .

TABLE 4

	Deactivator	Deactiv/Ti+Al (mol)	MW/ $\eta_{OH}$	$MI^{(A)}$	$MI^{(B)}$
Ex. 1	Propylen Glycol	2,6	38	0,40	0,45
Ex. 2	Propylen Glycol	2,86	38	0,75	0,90
Ex. 3	Dipropylen Glycol	3,5	67	0,40	0,50
Ex. 4 (comp)	---	---	---	0,40	3,0
Ex. 5 (comp)	Alkyldiethanol -amines	2,6	135-178	0,40	1,0

**CLAIMS**

1. A liquid-phase process for polymerizing  $\alpha$ -olefins of the formula  $\text{CH}_2=\text{CHR}$ , where R is H or an alkyl radical C1-C6, to produce a polymer that is soluble in the reaction medium, comprising the steps of:
  - a) continuously polymerising in liquid phase the  $\alpha$ -olefin in the presence of a catalyst based on a transition metal compound;
  - b) continuously withdrawing from step a) a solution of the polymer in the liquid reaction medium;
  - c) mixing in one or more mixing stages said solution of the polymer in the reaction medium with an organic compound having: at least a hydroxy group, a boiling point higher than  $150^\circ\text{C}$ , and a ratio between the molecular weight (MW) and the number of hydroxy groups ( $n_{\text{OH}}$ ) comprised between 20 and 100.
2. The process according to claim 1 wherein in step a) a solution of polybutene-1 in the reaction medium is obtained.
3. The process according to claims 1-2 wherein the polymerization step a) takes place in liquid phase in the presence of an inert hydrocarbon solvent.
4. The process according to claims 1-2 wherein liquid butene-1 is used as the reaction medium.
5. The process according to claims 1-2 wherein the polymerization temperature is generally kept at a value comprised in the range of from  $65$  to  $85^\circ\text{C}$  while the pressure is generally comprised between 8 and 40 bar.
6. The process according to claim 5 wherein the temperature is comprised between  $70$  and  $80^\circ\text{C}$  and the pressure is comprised between 12 and 25 bar.
7. The process according to claim 1 wherein a highly active catalyst of the Ziegler-Natta or metallocene type is used in step a).
8. The process according to claims 1-2 wherein the polymerization step a) is performed in one or more continuously stirred tank reactors, wherein a high-viscosity polymeric solution of polybutene-1 in butene-1 is formed.
9. The process according to claim 8 wherein the polymer concentration is kept to a value of less than 35% by weight.
10. The process according to claim 9 wherein the concentration of polybutene-1 in butene-1 is comprised between 10 and 30% by weight.

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11. The process according to claims 1- 2 wherein butene-1 is polymerized in the presence of up to 20% by weight, preferably 0,5-10% by weight based on butene-1, of another  $\alpha$ -olefin.
12. The process according to claim 1 wherein the deactivator compounds of step c) are characterized by a ratio between the molecular weight (MW) and the number of hydroxy groups (OH) comprised between 30 and 70.
13. The process according to claim 12 wherein the deactivator compounds are selected from propylen glycol, dipropylen glycol, glycerol, diethylen glycol, butandiol.
14. The process according to claims 1-13, wherein for deactivating a Ziegler-Natta catalyst comprising a Ti-based solid catalyst component and an Aluminum compound as an activator, the molar ratio deactivator/(Ti+Al) is higher than  $2/n_{OH}$ , wherein  $n_{OH}$  is the number of hydroxy groups of the deactivator compound.
15. The process according to claim 14 wherein the molar ratio deactivator/(Ti+Al) is comprised between  $3/n_{OH}$  and  $6/n_{OH}$ .
16. The process according to claim 1 wherein step c) is carried out in one or more mixing tanks placed in series.
17. The process according to claim 1 wherein step c) is carried out in a single deactivation apparatus equipped with a sequence of more mixing stages.
18. The process according to claim 17 wherein the deactivation apparatus comprises a stirring shaft provided with impellers in a number comprised between 2 and 20.
19. The process according to claims 17-18 wherein more mixing stages are formed along the shaft by the rotation of each impeller.
20. The process according to claims 17-19, wherein the impellers are equipped with radial blades fixed at the stirring shaft, said radial blades causing a radial flow inside each mixing stage.
21. The process according to claims 17-20, wherein a polymeric solution and a deactivator compound are continuously fed at the inlet of the apparatus and slowly flow through the sequence of mixing stages.
22. The process according to claims 17-21, wherein an axial piston-like flow is involved by the sequence of mixing stages along the shaft and by the complete

liquid filling of the apparatus.

23. The process according to claims 1-22, wherein after step c) the solution of polybutene in butene-1 is passed to a separation step, wherein the polybutene-1 is separated from the unreacted monomer, which is recovered and re-circulated to the polymerization step a).
24. The process according to claim 23, wherein the separation step is carried out by melt devolatilization using one or more volatilization chambers operating at a decreasing pressure.

**ABSTRACT**

A liquid-phase process for polymerizing  $\alpha$ -olefins of the formula  $\text{CH}_2=\text{CHR}$ , where R is H or an alkyl radical C1-C6, to produce a polymer that is soluble in the reaction medium, comprising the steps of:

- a) continuously polymerising in liquid phase the  $\alpha$ -olefin in the presence of a catalyst based on a transition metal compound;
- b) continuously withdrawing from step a) a solution of polymer in the liquid reaction medium;
- c) mixing in one or more mixing stages said solution of polymer in the reaction medium with an organic compound having: at least a hydroxy group, a boiling point higher than  $150^\circ\text{C}$ , and a ratio between the molecular weight (MW) and the number of hydroxy groups (OH) comprised between 20 and 100



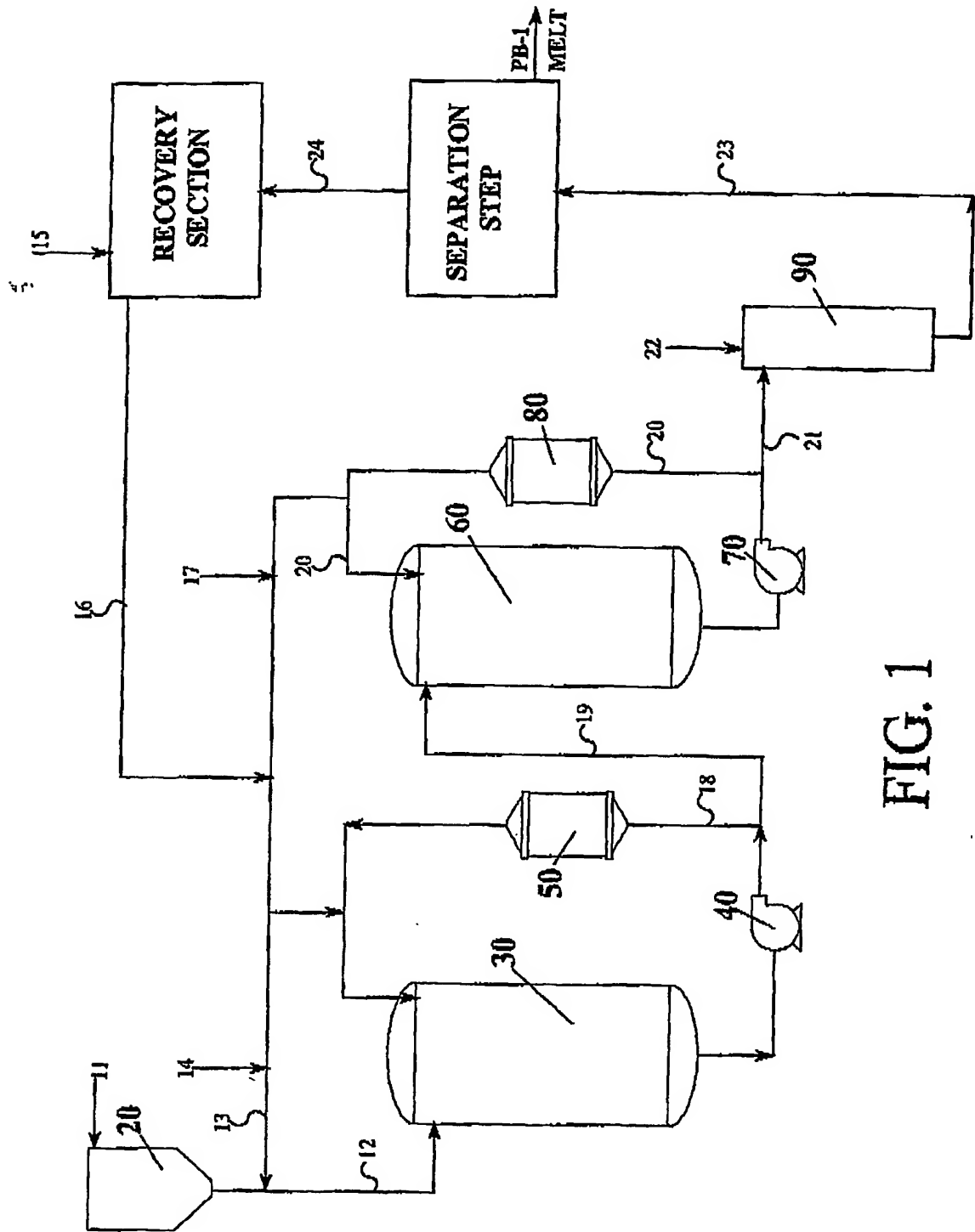
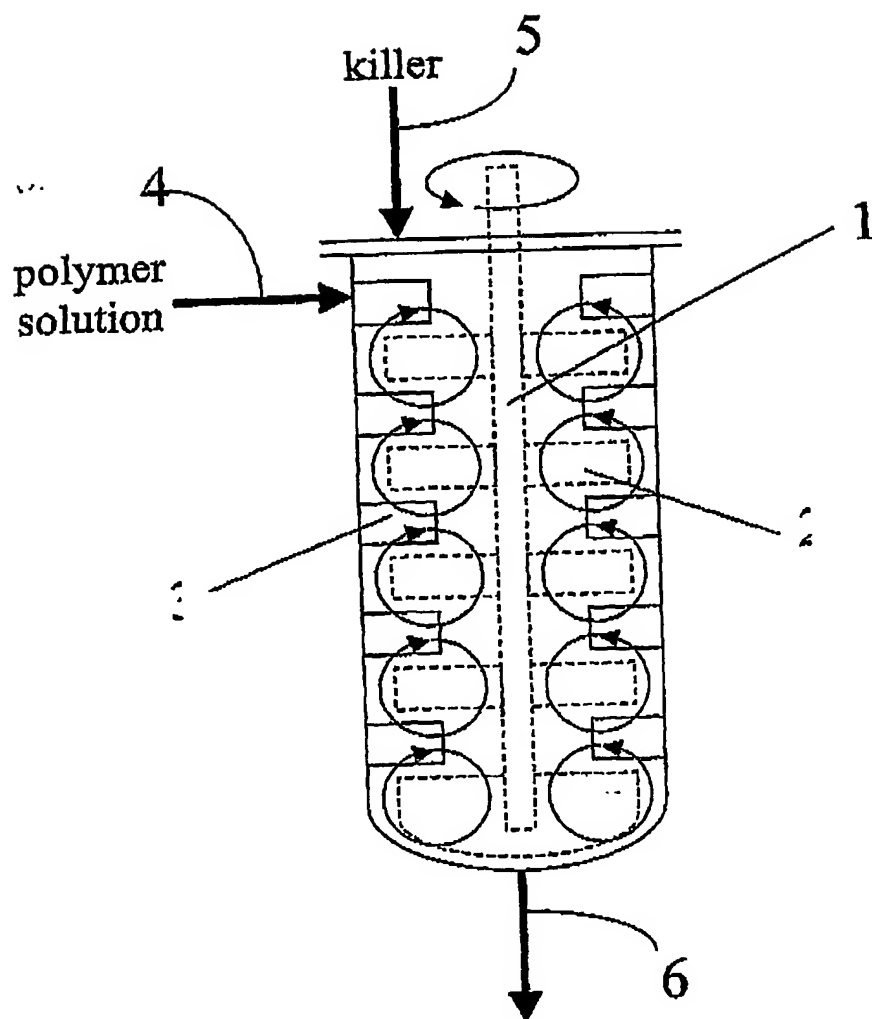


FIG. 1

**FIG. 2**

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